Studies in Azide Chemistry. Part III.[1] Polyfluorinated Azides from 1*H*- and 2*H*-Pentafluoropropene and Perfluorobut-2-yne

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Treatment of 1*H*-pentafluoropropene with sodium azide in dimethylformamide gave 1*H*-tetrafluoroprop-1-enyl azide; this product was also obtained, together with a compound tentatively identified as 1*H*,2*H*-pentafluoropropyl azide, when 1*H*-pentafluoropropene was treated with triethylammonium azide in *sym*-tetrachloroethane. The occurrence of a violent explosion prevented characterisation of the products from a reaction between 2*H*-pentafluoropropene and triethylammonium azide, but interaction of the latter with perfluorobut-2-yne was shown to yield 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide. Pyrolysis of 1*H*-tetrafluoroprop-1-enyl azide gave αβββ-tetrafluoropropionitrile and 2-fluoro-2-trifluoromethyl-2*H*-azirine.

HITHERTO only three † polyfluorovinyl azides appear to have been synthesised: perfluoroprop-1-enyl azide (I; X = Y = F), perfluoroisobut-1-enyl azide (I; X = CF_3, Y = F), and hexafluoro-1-methoxyisobut-1-enyl azide (I; X = CF_3, Y = OMe). Perfluoroprop-1-enyl azide is prepared by treatment of perfluoropropene with sodium [2]

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† An unsuccessful attempt to prepare $CFCl{:}CF{\cdot}N_3$ has been reported.[1]

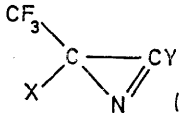
[1] Part II, R. E. Banks, D. Berry, M. J. McGlinchey, and G. J. Moore, *J. Chem. Soc.* (*C*), 1970, 1017.

[2] R. E. Banks and G. J. Moore, *J. Chem. Soc.* (*C*), 1966, 2304.

or triethylammonium [2-4] azide, and has been isolated [2] despite the fact that it decomposes steadily at room temperature into nitrogen and perfluoro-(2-methyl-2*H*-azirine) (II; X = Y = F). Neither of the other polyfluorovinyl azides has been isolated. Presumably perfluoroisobut-1-enyl azide is a transient intermediate in the reaction reported to occur between perfluoroisobutene and sodium azide in ethanol at 0°; [3] and hexafluoro-1-methoxyisobut-1-enyl azide is logically assumed to be the precursor of 3-methoxy-2,2-bis(trifluoromethyl)-2*H*-azirine (II; X = CF_3, Y = OMe) obtained from methyl perfluoroisobut-1-enyl ether and sodium azide at 0—25°.[5]

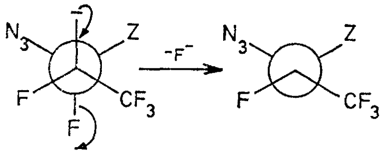
$CF_3\cdot CX=CY\cdot N_3$

(I)



(II)

1*H*-Tetrafluoroprop-1-enyl azide (I; X = F, Y = H), which is thermally stable at room temperature, has now been prepared by treatment of a *ca.* 95 : 5 mixture of *cis*- and *trans*-1H-pentafluoropropene with sodium azide in dimethylformamide or with triethylammonium azide in *sym*-tetrachloroethane. Use of the latter reagent also results in the formation of a product believed, on the basis of spectroscopic evidence, to be 1*H*,2*H*-pentafluoropropyl azide (*cf.* the formation of 2*H*-hexafluoropropyl azide from perfluoropropene and triethylammonium azide [2]). The magnitude of the n.m.r. H–F coupling constant (21·2 Hz) for the 1*H*-tetrafluoroprop-1-enyl azide isolated is indicative of a *trans* arrangement of the vinylic fluorine and hydrogen nuclei; [6] this geometry would result from *trans*-elimination of fluoride from the preferred conformer of the carbanion presumed (see refs. 1 and 2) to be formed in a reaction between *cis*-1*H*-pentafluoropropene and an ionic azide, and accords with the formation of only *trans*-perfluoroprop-1-enyl azide from perfluoropropene under similar circumstances.[2]



(Z = H or F)

In keeping with knowledge of the thermal decomposition of hydrocarbon vinyl azides containing a $:CH\cdot N_3$ group,[7] flow pyrolysis of 1*H*-tetrafluoroprop-1-enyl azide at 315°/*ca.* 2 mmHg gives αβββ-tetrafluoropropionitrile (84%) and 2-fluoro-2-trifluoromethyl-2*H*-azirine (II; X = F, Y = H) (12%). No attempt was made to determine if some or all of the nitrile is formed by rearrangement of 2-fluoro-2-trifluoromethyl-2*H*-azirine formed initially (*cf.* thermal rearrangement of 2-phenyl-2*H*-azirine to phenylacetonitrile and indole [8]).

The appreciable difference in thermal stability between perfluoroprop-1-enyl azide and 1*H*-tetrafluoroprop-1-enyl azide prompted an attempt to prepare another polyfluorovinyl azide not containing an α-fluorine substituent. Accordingly, a reaction was carried out between perfluorobut-2-yne and triethylammonium azide in *sym*-tetrachloroethane and found to yield 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide (I; X = H, Y = CF_3) (21%), which is stable up to at least 60°. Although good elemental analyses (C, H, and N) have been obtained by standard procedures for a number of acyclic [1,2] (including 1*H*-tetrafluoroprop-1-enyl azide) and heteroaromatic [9] polyfluoro-azides, only incorrect and irreproducible results were achieved with 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide (the same difficulty has been experienced with 2*H*-hexafluorobut-2-enyl azide [10]), so its identification rests on analysis of spectroscopic data (i.r., n.m.r., and mass); the n.m.r. coupling constants observed [$J(CF_3,CF_3)$ *ca.* 1·7, $J(vic\text{-}CF_3,H)$ *ca.* 0·7 Hz] indicate [6,11,12] that the trifluoromethyl groups are *trans*-disposed, which accords with the expected *trans*-addition of the elements of hydrazoic acid across the triple bond in perfluorobut-2-yne *via* a nucleophilic mechanism.[11]

Since 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide contains no β-fluorine substituent, an attempt was made to prepare 2*H*-tetrafluoroprop-1-enyl azide (I; X = H, Y = F), to determine how the thermal stability of perfluoroprop-1-enyl azide is affected by substitution of the β-fluorine by hydrogen. Thus, 2*H*-pentafluoropropene, which, like 1*H*-pentafluoropropene,[13] undergoes nucleophilic attack at the terminal olefinic carbon atom,[13,14] was treated with triethylammonium azide in *sym*-tetrachloroethane. The volatile product seemed quite stable at room temperature, and was distilled to give a mixture, b.p. 65—75°, containing (by i.r. and g.l.c. analysis) an azide or azides and a fluoro-olefin (possibly $CF_3\cdot CH_2\cdot CF_2\cdot N_3$ and $CF_3\cdot CH{:}CF\cdot N_3$) together with trichloroethylene (from dehydrochlorination of the solvent by triethylamine [2]). These components were separated by g.l.c. (column heated to 60°), but when samples of the first two were being transferred simultaneously from the collection traps to a vacuum system a violent explosion occurred, which destroyed the

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[3] I. L. Knunyants and E. G. Bykhovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1960, **131**, 1338.

[4] C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, 1965, **87**, 3716.

[5] C. G. Krespan, *J. Org. Chem.*, 1969, **34**, 1278.

[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1966, vol. 2.

[7] J. H. Boyer, W. E. Krueger, and G. J. Mikol, *J. Amer. Chem. Soc.*, 1967, **89**, 5504; G. Smolinsky and C. A. Pryde, *J. Org. Chem.*, 1968, **33**, 2411; J. S. Meek and J. S. Fowler, *ibid.*, p. 3418; K. Isomura, M. Okada, and H. Taniguchi, *Tetrahedron Letters*, 1969, 4073.

[8] K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, 1968, 3499.

[9] R. E. Banks and G. R. Sparkes, publication in preparation.

[10] R. E. Banks and D. Berry, unpublished work.

[11] W. R. Cullen, D. S. Dawson, and G. E. Styan, *Canad. J. Chem.*, 1965, **43**, 3392, and references cited therein.

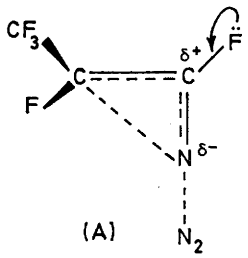
[12] R. D. Chambers and A. J. Palmer, *Tetrahedron*, 1969, **25**, 4217.

[13] R. Fontanelli, G. Paschetta, M. Tacchi Venturi, and D. Sianesi, *Ann. Chim. (Italy)*, 1969, **59**, 211.

[14] R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, personal communication.

samples and also a large part of the vacuum system. The investigation was therefore discontinued.

Apart from the observation that the presence of large *cis*-disposed substituents results in loss of nitrogen and azirine formation at relatively low temperatures [*e.g.*,[15,16] *cis*-PhC(N$_3$)⁚CHPh and *cis*-PhC(N$_3$)⁚CH·CO$_2$Me are unstable at room temperature], the factors influencing the thermal stability of a vinyl azide do not seem to have been assessed. In addition, the mechanism of thermal decomposition has not been established.[17] As pointed out previously,[2,4] thermal conversion of perfluoroprop-1-enyl azide into perfluoro-(2-methyl-2*H*-azirine) can be envisaged to occur *via* formation and subsequent decomposition of a triazole, through the intermediacy of perfluoroprop-1-enylnitrene, or by ring-closure with concerted loss of nitrogen. As expected,[17,18] no evidence was found for a triazole intermediate, and the ease with which the azide decomposes compared with 2*H*-hexafluoropropyl azide[1] seems to favour the concerted mechanism; the failure to observe C–H insertion during decomposition of perfluoroprop-1-enyl azide in the presence of an excess of cyclohexane does not, however, rule out the nitrene mechanism, since the entropy of activation of intramolecular ring-closure would be more favourable than that of intermolecular insertion. On the basis of a concerted mode of decomposition, it seems that the relative stabilities of perfluoroprop-1-enyl azide and 1*H*-tetrafluoroprop-1-enyl or 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide could be ascribed in part to stabilisation of the transition state (A) in the case of the perfluorinated compound by electromeric release of electron density by the α-fluorine; the same suggestion applies in the case of perfluoroisobut-1-enyl azide, and a similar but more powerful effect could be invoked for hexafluoro-1-methoxyisobut-1-enyl azide in the light of the presence of an α-methoxy-function. It would also appear reasonable to ascribe the differences in rates of decomposition partly to appreciable differences in ground-state stabilities, and the more unstable azides could contain 'strained' C⁚C bonds brought about by the combined electronegativities of their substituents.[19]



(A)

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer spectrophotometer model 257, n.m.r. spectra with a Perkin-Elmer R10 instrument operating at 35° and 56·46 (^{19}F) or 60 (^{1}H) MHz, and mass spectra with an A.E.I. MS/2H or MS902 spectrometer. Molecular weights were determined by Regnault's method unless stated otherwise.

Triethylammonium azide was prepared and used essentially as described by others.[4] 1*H*-Pentafluoropropene (a *ca.* 95 : 5 *cis–trans* mixture) was synthesised by dehydrofluorination of 1*H*,2*H*-hexafluoropropane, procured by hydrogenation of commercial hexafluoropropene.[20] 2*H*-Pentafluoropropene was prepared by dehydroiodination of 1,1,3,3,3-pentafluoro-1-iodopropane obtained by photolysis of trifluoroiodomethane with commercial vinylidene fluoride.[21] Perfluorobut-2-yne was used directly from a commercial cylinder.

CAUTION. Robust face shields (which also provide neck protection), blast screens, and guard tubes should be used, where appropriate, during the manipulation of fluoro-azides.

Reactions of 1H-*Pentafluoropropene*.—(a) *With sodium azide*. 1*H*-Pentafluoropropene (13·2 g., 0·10 mole) was condensed *in vacuo* into a cold (−196°), thick-walled, Pyrex tube (300 ml.) containing sodium azide (13·0 g., 0·20 mole) and dimethylformamide (120 ml.). The tube was sealed, *in vacuo*, and placed in a stout mild steel guard tube while still cold; the guard tube was stored at room temperature for 17 days, during which time it was frequently shaken gently. The volatile product was pumped from the reaction vessel, condensed at −196°, and fractionated *in vacuo* to give 1*H*-pentafluoropropene (0·8 g., 6·1 mmoles; 6% recovery), identified by i.r. spectroscopy, and 1H-*tetrafluoroprop*-1-*enyl azide* (4·1 g., 26 mmoles, 28% based on 1*H*-pentafluoropropene consumed) (Found: C, 23·4; H, 1·0; N, 26·8%; *M*, 154. $C_3HF_4N_3$ requires C, 23·2; H, 0·65; N, 27·1%; *M*, 155), b.p. 56—57°/743 mmHg, $\lambda_{max.}$ (vapour) 3·20vw (⁚C–H str.), 4·72vs (azide asym. str.), 5·83m, 5·88m (doublet assigned to C=C str., the splitting presumably arising from a Fermi resonance interaction), 7·23vs, 7·63s, 7·80vs, 7·92vs (doublet), 8·33vs, 8·55vs (doublet), 8·95m, 9·26s, 9·96w, 10·42m (⁚C–H def.), 11·49s, 12·05w, 13·80m, 13·89m, 14·00m (triplet, CF$_3$ def.), and 15·75m μm., δ_F (CF$_3$·CO$_2$H interchange) −4·2 {CF$_3$, doublet [*J*(*gem*-CF$_3$,F) 12·9] of doublets [*J*(CF$_3$,H) 0·9 Hz]} and +71·4 {CF$_3$·C*F*, doublet [*J*(H,F) 21·2 Hz] of quartets} p.p.m., δ_H (benzene interchange) +0·6 p.p.m. (doublet of quartets). The mass spectrum of the azide showed a strong parent ion [$C_3HF_4N_3^+$, 42% (*m*/*e* 155)] and other prominent peaks at *m*/*e* 127 ($C_3HF_4N^+$, 16%), 108 ($C_3HF_3N^+$, 16%), 100 ($C_2F_4^+$, 41%), 69 (CF_3^+, 100%), 58 (C_2HFN^+, 29%), 50 (CF_2^+, 11%), 31 (CF^+, 73%), and 28 (N_2^+, 36%).

(b) *With triethylammonium azide*. A reaction was carried out between 1*H*-pentafluoropropene (13·2 g., 0·10 mole) and triethylammonium azide (30·0 g., 0·21 mole) in *sym*-tetrachloroethane (130 ml.) as described in (a) but for a period of 1 month. Fractionation of the volatile product afforded 1*H*-pentafluoropropene (0·5 g., 3·8 mmoles, 4% recovery) and a mixture (4·90 g.) that was separated by

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[15] F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077.

[16] A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 1968, **90**, 2869.

[17] G. Smolinsky, *J. Org. Chem.*, 1962, **27**, 3557; G. R. Harvey and K. W. Ratts, *ibid.*, 1966, **31**, 3907; J. S. Meek and J. S. Fowler, *J. Amer. Chem. Soc.*, 1967, **89**, 1967; *J. Org. Chem.*, 1968, **33**, 3418; G. Smolinsky and C. A. Pryde, *ibid.*, 2411.

[18] P. A. S. Smith, 'The Chemistry of Open-chain Nitrogen Compounds,' Benjamin, New York, vol. 2, p. 243.

[19] W. A. Bernett, *J. Org. Chem.*, 1969, **34**, 1772.

[20] D. Sianesi and R. Fontanelli, *Ann. Chim.* (*Italy*), 1965, **55**, 850.

[21] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1954, 923.

g.l.c. (4 m. silicone oil MS550–Celite, 40°) into 1*H*-tetrafluoroprop-1-enyl azide (2·44 g., 15·7 mmoles, 16% based on 1*H*-pentafluoropropene consumed), identified by i.r. and n.m.r. spectroscopy and g.l.c. retention time, material believed to be essentially 1*H*,2*H*-pentafluoropropyl azide (0·56 g., *ca.* 3%) [$\lambda_{max.}$ (vapour) 4·67 μm. (strong, complex; N_3 asym. str.), *m/e* of 175 ($C_3H_2F_5N_3^+$, 3%), 147 ($C_3H_2F_5N^+$, 11%), 102 ($C_2H_2F_4^+$, 35%), 100 ($C_2F_4^+$, 63%), 97 ($C_2H_2F_3N^+$, 21%), and 69 (CF_3^+, 100%)], and a residue containing (by i.r. spectroscopy) trichloroethylene.

Pyrolysis of 1H-*Tetrafluoroprop*-1-*enyl Azide*.—The vapour of the azide (0·73 g., 4·71 mmoles) was passed (1·9 hr.) at *ca.* 2 mmHg pressure through a 70 × 1·0 cm. copper tube heated to 315° over 40 cm. of its length. The product, collected in two cold (−196°) traps, was fractionated to give αβββ-tetrafluoropropionitrile (0·50 g., 3·94 mmoles, 84%), identified by comparison of its i.r. spectrum with that of an authentic sample and by n.m.r. spectroscopy [δ_F ($CF_3{\cdot}CO_2H$ interchange) +2·0 {CF_3, doublet [$J(CF_3,F)$ 14·4] of doublets [$J(CF_3,H)$ 5·1 Hz]} and +131·2 {CH*F*, doublet [*J*(*gem*-H,F) 43·8 Hz] of quartets} p.p.m., δ_H (benzene interchange) +1·3 p.p.m. (doublet of quartets)] and 2-*fluoro*-2-*trifluoromethyl*-2H-*azirine* (0·07 g., 0·55 mmole, 12%) (Found: C, 28·3; H, 0·9; N, 10·5%; *M*, 128. C_3HF_4N requires C, 28·3; H, 0·8; N, 11·0%; *M*, 127), $\lambda_{max.}$ 5·60 μm. (C=N str.). In a similar experiment at 150°, the azide was recovered almost quantitatively.

Reaction of 2H-*Pentafluoropropene with Triethylammonium Azide*.—2*H*-Pentafluoropropene (13·2 g., 0·10 mole), triethylammonium azide (30·0 g., 0·21 mole), and *sym*-tetrachloroethane (130 ml.) were kept in a Pyrex ampoule (300 ml.) encased in a steel guard tube at 0° for 60 hr. The volatile product was fractionated *in vacuo* to yield (fractions analysed by i.r. spectroscopy and g.l.c.) (i) (−196° trap) 2*H*-pentafluoropropene (1·1 g., 8·3 mmoles, 8% recovery), (ii) (−72° trap) a mixture (8·3 g.) showing both azide and olefinic absorptions in the i.r. at 4·65—4·74s (complex) and 5·84m μm., respectively, and containing trichloroethylene, and (iii) (−23° trap) a mixture (16·3 g.) of trichloroethylene and *sym*-tetrachloroethane. Distillation of the −72° fraction in a semi-micro Vigreux still gave a mixture (4·7 g.), b.p. 65—75°, containing (by g.l.c.) trichloroethylene and two other components; the latter were isolated by g.l.c. (4 m. silicone oil MS550–Celite; 60°) but the samples were destroyed by a violent explosion that occurred when the contents of the glass g.l.c. traps (used at −72° for collection purposes) were being transferred into a vacuum system for examination.

Reaction of Perfluorobut-2-*yne with Triethylammonium Azide*.—The acetylene (16·2 g., 0·10 mole) was condensed, *in vacuo*, into a Pyrex tube (300 ml.) containing triethylammonium azide (30·0 g., 0·21 mole) and *sym*-tetrachloroethane (130 ml.). The tube was sealed, shaken vigorously while it warmed to *ca.* −10°, and stored at 0° for 17 hr. Distillation of the volatile product gave 3,3,3-trifluoro-1-trifluoromethylprop-1-enyl azide (4·3 g., 21 mmoles, 21%), b.p. 59°/753 mmHg, $\lambda_{max.}$ (vapour) 4·67s (N_3 asym. str.) and 5·95m (C=C str.) μm., trichloroethylene (6·3 g.) with the expected i.r. spectrum, and a residue (15 g.) containing trichloroethylene and *sym*-tetrachloroethane. Several combustion analyses were carried out on the propenyl azide but the results were non-reproducible and grossly incorrect (*e.g.* Found: C, 12·6, 19·5; H, 1·9, 2·5; N, 43·4, 41·2. Calc. for $C_4HF_6N_3$: C, 23·4; H, 0·5; N, 20·5%); the high nitrogen values were caused by incomplete destruction of the samples in the Dumas-type train employed, since the gas collected in the nitrometer was shown by i.r. spectroscopy to contain fluorocarbon material. The ^{19}F n.m.r. spectrum ($CF_3{\cdot}CO_2H$ interchange) of the azide was consistent with the structure proposed, showing two absorptions of equal intensity at −17·9 {C*F*$_3$·CH, doublet [*J*(*gem*-CF_3,H) 7·6] of quartets [$J(CF_3,CF_3)$ *ca.* 1·7 Hz]} and −7·4 {C*F*$_3$·CN_3, doublet [$J(CF_3,H)$ *ca.* 0·7 Hz] of quartets} p.p.m.; the ^1H spectrum showed a quartet of quartets at 0·95 p.p.m. to high field of external benzene. The principal peaks (rel. abund. ⩾10%) in the mass spectrum of the azide occurred at *m/e* values of 96 ($C_2HF_3N^+$, 26%), 69 (CF_3^+, 71%), 61 (25%), 43 (HN_3^+, 100%), and 28 (N_2^+, 38%); a peak at *m/e* 205 ($C_4HF_6N_3^+$, 5%) corresponded to the parent ion.

One of us (M. J. M.) thanks the S.R.C. for a studentship.

[0/398 *Received, March* 13*th*, 1970]